BASF and acetylene

50 Years of Natural Gas based Acetylene Production - now the only Clean Technology for Acetylene Production

Dr. Vicari, 6th International Freiberg Conference on IGCC & XtL Technologies, Coal Conversion and Syngas, 19-22 May 2014, Dresden/Radebeul, Germany
BASF and acetylene
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- How to make acetylene
- The closed water-quench process
- Some safety aspects
- Typical Plant setup
BASF and acetylene
How to make acetylene

- Partial Oxidation
  - BASF Sachsse-Bartholomé
    - BASF (D/USA) – Ukraine, China …
  - Montecatini process
    - Lonza (CH)

- Electric arc – plasma process
  - Ashland / ISP Marl (D)

- Steam-cracker - byproduct: worldwide

- Calcium carbide:
  - China, Japan, former USSR, Eastern Europe
BASF and acetylene
Partial oxidation of hydrocarbons

- Partial oxidation (~ 60 % methane)
  \[ 2\text{CH}_4 + 0.5\text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2 \]
  \[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \]
  Flame, exothermal; Temp. ~ 1500°C

- Acetylene Formation
  \[ 2\text{CH}_4 \rightarrow 1500^\circ\text{C} \rightarrow \text{C}_2\text{H}_2 + 3\text{H}_2 \]
  residual methane 4%
  residence time a couple of 1/1000 sec
BASF and acetylene
Technology of premixed combustion with reaction quenching
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Overview

Generation

\[ \text{CH}_4 + \text{O}_2 \rightarrow \text{C}_2\text{H}_2 + \text{CO} + \text{H}_2 + \text{CO}_2 + \text{H}_2\text{O} + \text{HA} + \text{aromates} + \text{soot} \]

Separation

AOG : CO + H\(_2\) + CO\(_2\) + ...

CH\(_4\)

O\(_2\)

H\(_2\)O + soot + ...

C\(_2\)H\(_2\)

HA + aromates + ...
BASF and acetylene
BASF’s new closed water quench

Acetylene water quench process (AWP)
a) Preheaters; b) Acetylene burner; c) Cooling column; d) Electrofilter; e) Soot decanter; f) Cooling tower

3 burners per cooling column

Cracked gas to compression (30°C)

(Tabes hydrocarbons end up in wastewater and HA-gas)

No emissions

Soot separation by wastewater pre-treatment unit

Natural gas

Fuel

Oxygen

WWTP
### Emission open water quench Process

<table>
<thead>
<tr>
<th>Compound</th>
<th>g/t Ac</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>667</td>
</tr>
<tr>
<td>Methane</td>
<td>141</td>
</tr>
<tr>
<td>Ethane</td>
<td>20</td>
</tr>
<tr>
<td>Ethylene</td>
<td>36</td>
</tr>
<tr>
<td>Acetylene</td>
<td>6,203</td>
</tr>
<tr>
<td>higher Acetylenes</td>
<td>1,056</td>
</tr>
<tr>
<td>Benzene</td>
<td>162</td>
</tr>
<tr>
<td>Naphthaline</td>
<td>14</td>
</tr>
</tbody>
</table>
Figure 13. BASF acetylene process — N-methylpyrrolidone absorption section
a) Compressor; b) Prescrubber; c) Acetylene stripper; d) Main scrubber; e) Stripper; f) Vacuum column; g) Vacuum stripper; 
h) Side column; i) Condenser; j) Vacuum pumps
BASF and acetylene
Usage of acetylene off-gas (AOG)

- Methanol
  - Methanol to chemicals
  - Methanol to olefins
- Acetic acid
  - Vinyl acetate
- Separation for production of H₂ and CO
  - Any chemical, which requires H₂ and/or CO
- Ammonia / CO₂
  - Urea
  - Fertilizers
- Fuel: not recommended especially if cheap fuels are substituted
How to make acetylene

The closed water-quench process

Some safety aspects

Typical Plant setup
BASF and acetylene
e.g. safety aspect intrusion of air in vacuum sec.

- Scenario
  - E.g. rupture of a 25 mm nozzle in the vacuum section at 200 mbar(abs.) for example by a crane during maintenance work
    - Intrusion of 318 kg/h air (52 Nm³/h O₂)
    - Vacuum-Compressor feeds 3,000 Nm³/h acetylene
  - Oxygen content in acetylene is then 1.73 Vol.%
  - Limit is 1 Vol.%
    - at > 1 Vol.%
      - Sargent diagram no longer valid
      - Decomposition barriers no longer working
      - Instead of deflagration immediate detonation may occur
BASF and acetylene
Explosion regime acetylene/air

- Detection and countermeasures in SIL 3 quality
- Counter measure: dilution and flaring

0.8 bar (abs.)
1.0 bar (abs.)
1.2 bar (abs.)
BASF and acetylene
Autodecomposition of gas-mixtures (acetylene and higher acetylenes)

**Approach**

- Use of critical partial-pressures of pure components

<table>
<thead>
<tr>
<th>Compound</th>
<th>Decomposition Pressure [bar(a)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>1.4</td>
</tr>
<tr>
<td>Methylacetylene</td>
<td>1.8</td>
</tr>
<tr>
<td>Vinylacetylene</td>
<td>0.4</td>
</tr>
<tr>
<td>Diacetylene</td>
<td>0.2</td>
</tr>
</tbody>
</table>

- **Combination** : like lower explosion limit (LeChatelier Formula)

\[
p_{\text{Mixture}}^* = \frac{1}{\sum \frac{x_i}{p_i^*}}
\]
### BASF and acetylene

#### Autodecomposition of gas mixtures (Acetylene and higher acetylenes)

- Example: higher acetylene off-gas **before** dilution

<table>
<thead>
<tr>
<th></th>
<th>$p_{\text{crit}}$ [bar$_a$]</th>
<th>Vol.%</th>
<th>$x_i/p_i$</th>
<th>$p_{\text{crit, Ac}}/p_{\text{crit}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>1.4</td>
<td>33.6</td>
<td>0.240</td>
<td>1</td>
</tr>
<tr>
<td>Methylacetylene</td>
<td>1.8</td>
<td>2.3</td>
<td>0.013</td>
<td>0.778</td>
</tr>
<tr>
<td>Vinylacetylene</td>
<td>0.4</td>
<td>10.8</td>
<td>0.270</td>
<td>3.5</td>
</tr>
<tr>
<td>Diacetylene</td>
<td>0.2</td>
<td>53.3</td>
<td>2.665</td>
<td>7</td>
</tr>
<tr>
<td>Dilution Gas</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Critical deflagration pressure**

$$0.314 \text{ bar}_a$$
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Situation in acetylene recovery unit

Figure 13. BASF acetylene process — N-methylpyrrolidone absorption section
a) Compressor; b) Prescrubber; c) Acetylene stripper; d) Main scrubber; e) Stripper; f) Vacuum column; g) Vacuum stripper;
h) Side column; i) Condenser; j) Vacuum pumps
### BASF and acetylene

**Autodecomposition of gasmixtures (Acetylene and higher acetylenes)**

- Example: higher acetylene off-gas after dilution

<table>
<thead>
<tr>
<th></th>
<th>$p_{crit}$ [bar$_a$]</th>
<th>Vol.%</th>
<th>$x_i/p_i$</th>
<th>$p_{crit, Ac}/p_{crit}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>1.4</td>
<td>6.0</td>
<td>0.043</td>
<td>1</td>
</tr>
<tr>
<td>Methylacetylene</td>
<td>1.8</td>
<td>0.4</td>
<td>0.002</td>
<td>0.778</td>
</tr>
<tr>
<td>Vinylacetylene</td>
<td>0.4</td>
<td>1.9</td>
<td>0.048</td>
<td>3.5</td>
</tr>
<tr>
<td>Diacetylene</td>
<td>0.2</td>
<td>9.5</td>
<td>0.475</td>
<td>7</td>
</tr>
<tr>
<td>Dilution Gas</td>
<td>82.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Critical deflagration pressure** 1.762 bar$_a$
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Acetylene plant in Geismar

- 50,000 t/a
- 8200 h/a
- 6 burner
- 2 burner trains
- 2 compressors
- 1 separation unit
BASF and acetylene
Acetylene plant in Geismar
BASF and acetylene
Conclusion

- Acetylene production and use for intermediate feedstock is based on 75 Years experience.

- High safety standards and open communication regarding safety issues are assured worldwide

- BASF closed water-quench process offers the only proven and clean access to acetylene based on natural gas
BASF and acetylene
Acknowledgement

Contributions to this presentation, made by

- Dr. Matthias Kern, Research Engineer,
- Klaus-Peter Rieser, Global Communications Intermediates,
- Dr. Hans-Peter Schildberg, Expert Gaseous Explosion Safety
- Dr. Christian Weichert, Senior Manager Global Technology